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Abstract. In this study, the distribution of Cu element in a Al (99.9996% purity)-0.3%Cu alloy cold rolled to 98% has been characterized in detail by using three-dimensional atom probe (3DAP) and ChemiSTEM techniques. The cold rolled structure is a typical high strain lamellar structure with an average boundary spacing of 200 nm, indicating a strong role of the small amount of Cu element in stabilizing the microstructure to form the fine scale structure. A heavy segregation of Cu element in the lamellar boundaries of high angles has been observed and the Cu concentration in the boundaries can be as high as 20 times of the nominal concentration of the alloy, which is considered as the main reason for a formation of a stable nanoscale lamellar structure.

1. Introduction

Nanostructured and ultrafine-grained metals have in general high strength but low ductility and poor thermal stability [1-5]. Introducing dispersion fine particles can facilitate the generation of nanostructured metals by high strain deformation even in the case when the matrix is of ultrahigh purity [6-14]. Another way to stabilize nanostructured metals is to use alloying elements that may form boundary segregation or precipitates in the nanostructured metals. Different alloying elements may have different efficiency in stabilizing nanostructured metals [15, 16]. In our present studies [17-18], we found that a nanostructured lamellar structure with an average lamellar boundary spacing of 200 nm can be produced after 98% cold rolling in an Al-0.3%Cu alloy with an ultra-high pure Al matrix (99.9996%) and an addition of a small amount (0.3wt%) Cu. In this study, the distribution of the Cu element is characterized in detail to understand the mechanism of Cu in stabilizing the nanostructure.

2. Material and Experimental

An Al-0.3%Cu alloy ingot was produced by using an ultra-high pure (99.9996%) Al base material and addition of 0.3wt.% oxygen free high conductivity (OFHC) Cu. The ingot was cold rolled to a thickness reduction of 98% (corresponding to ε_{vM}=4.5). The microstructure of the cold rolled sample was characterized from the longitudinal section (containing the normal direction, ND, and rolling

direction, RD) by means of transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The TEM foils were prepared by twin jet electropolishing and examined in a JOEL JEM2100 electron microscope operating at 200 kV. An online Kikuchi-line analysis system installed in the microscope was used to measure the orientations and misorientations [19]. Dislocation density was calculated based on average dislocation spacing obtained by intersection method and sample thickness determined by CBED method. The TEM foils were also characterized on an FEI Titan G2 60-300 ChemiSTEM with a super X energy dispersive spectrometer (EDS) system. SEM samples were mechanically ground to 4000 SiC paper followed by electropolishing in a 10% perchloric acid and ethanol solution at -20°C. SEM observations were conducted with an FEI Nova400 nanoSEM equipped with a high sensitive backscattering electron (BSE) detector. A CAMECA LEAP4000HR three dimensional atom probe (3DAP) was applied to characterize the element distribution in the cold rolled sample. Needle specimens for 3DAP were prepared by electropolishing using a 5% perchloric acid and ethanol solution. The 3DAP experiments were done with a specimen temperature of 50K, voltage pulse rate of 200 kHz and ion collection rate of 0.5%.

3. Results and Discussion

3.1. Microstructure

Figure 1 shows the microstructure formed in the 98% cold rolled sample. A typical lamellar structure is developed, which is composed of extended lamellar boundaries along the RD and short boundaries interconnecting the lamellar boundaries. The lamellar boundaries have an average boundary spacing of 200 nm. A previous study showed that the ultra-high pure Al (99.9996%) [6] has a very poor thermal stability during cold rolling and dynamic recrystallization may take pace when the rolling strain is above 30%. The addition of 0.3% Cu enabled the generation of the nanoscale lamellar structure [17,18]. The lamellar boundary spacing is comparable with that reported for commercial purity Al (99.2 – 99.5% pure) [20-23] deformed by accumulative roll bonding (ARB) to 6 cycles. Note that the lamellar boundary spacing obtained in the Al-0.3%Cu alloys is finer than that (700-1000 nm) reported for a 99.99% pure Al [24] processed by 6 ARB cycles and that (230 nm) for an Al-1%Si alloys cold rolled to 98% [6]. Clearly the addition of a small amount Cu facilitated the formation of a fine scale lamellar structure. In figure 1a, small particles are seen at a few lamellar boundaries. However, SEM-BSE observations over relatively larger areas showed that most of the lamellar boundaries are free of particles in the 98% cold rolled state, as shown in figure 1b.

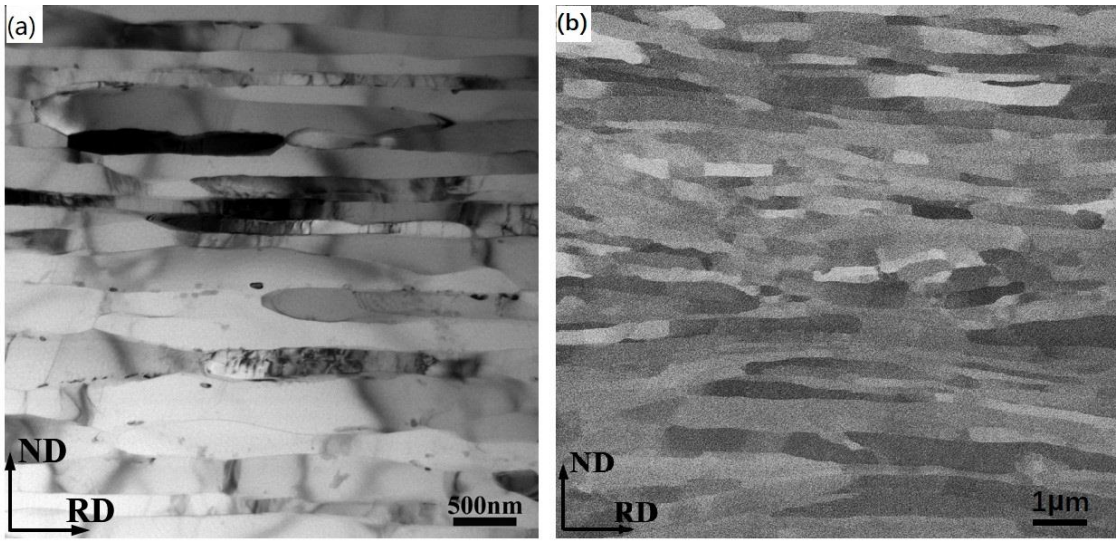

Figure 1. TEM (a) and SEM-BSE (b) images showing the nanoscale lamellar structure of Al-0.3%Cu alloy cold rolled to 98%.

The density of dislocations presented in the volumes between lamellar and interconnecting boundaries was measured to be 1.75×10^{14} m^{-2}, which is a few times higher than those observed in the ARB processed commercial purity Al 1100 [23] and 99.99% purity Al [24], probably due to the pinning effect of solid solute Cu atoms in the matrix.

3.2. Cu distribution

Figure 2a shows a 3DAP map of the 98% cold rolled sample. The red dots in the map represent the Cu atoms. For clarity, the Al atoms are not shown in the map. The volume analyzed is $34\times34\times309$ nm^3. In figure 2a, there is a line with high concentration of Cu element. Orientation analysis using the method proposed by reference [25] showed that the line corresponds to a high angle lamellar boundary. The details of Cu distribution within the marked column in (a) is shown in figure 2b. Evidently, the number of Cu atoms at the boundary is much larger than that in the matrix. The Cu concentration in the column was quantified along a distance from the top to bottom and is shown in figure 2c. It is seen that the Cu concentration at the lamellar boundary can be higher than 3at.% (about 7wt.%), which is higher than 20 times of the nominal concentration of the alloy.

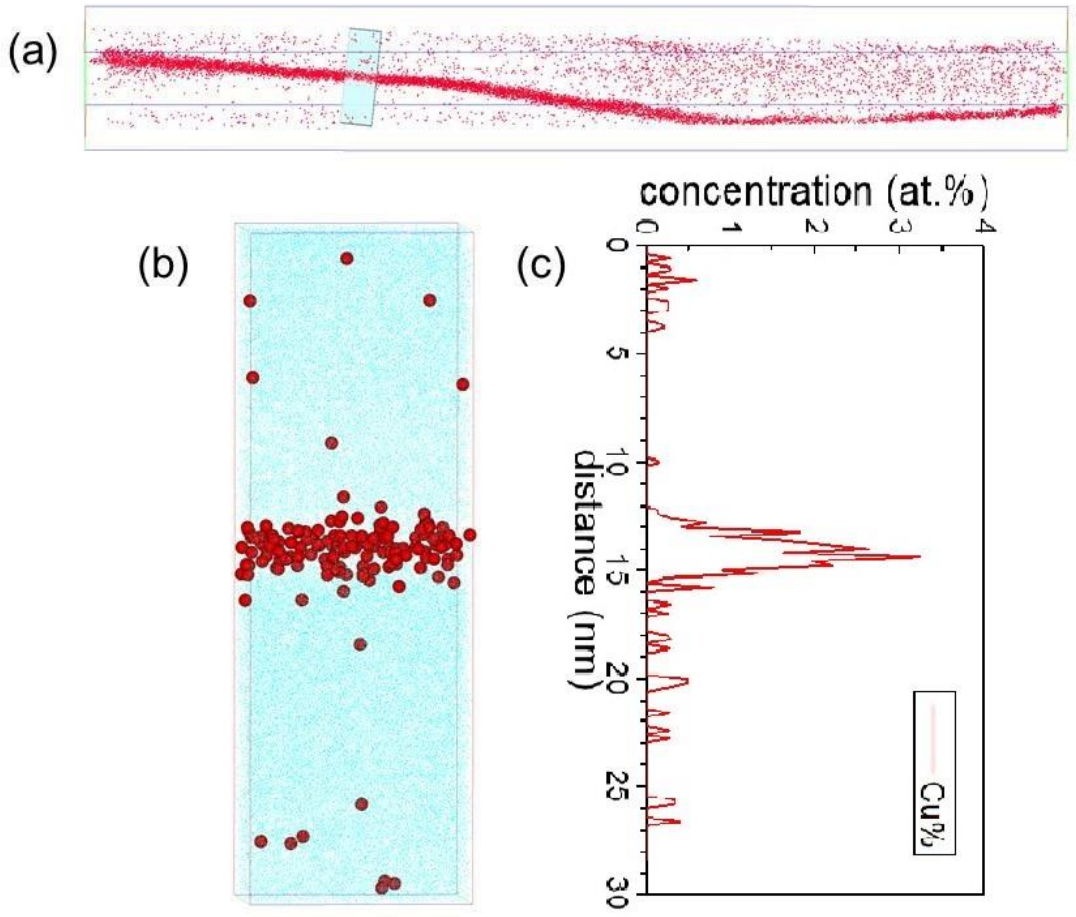

Figure 2. Distribution of Cu atoms (in red color) in the 98% cold rolled Al-0.3Cu alloy. (a) 3D reconstructed map of Cu atoms; (b) distribution of Cu atoms within the column marked in a); (c) distribution of Cu concentration versus distance in (b).

To show the Cu distribution over larger areas, EDS mapping was conducted in the FEI Titan ChemiSTEM. One example of the EDS mapping results is shown in figure 3, in which the corresponding TEM image of the mapped area is shown. The misorientation angles across the lamellar boundaries seen in the area were measured and are indicated in figure 3. From the EDS map, it is seen that there are some traces of high concentration of Cu elements, which are well related to the lamellar boundaries. However, it should be noted that not all the boundaries have Cu segregation. For example, the only low angle lamellar boundary (8.9°) does not show a clear segregation of Cu on the EDS map. Furthermore, the interconnecting boundaries, which are often of low misorientation angles, show no Cu segregation. These observations indicate a possible effect of boundary misorientation on the segregation of Cu.

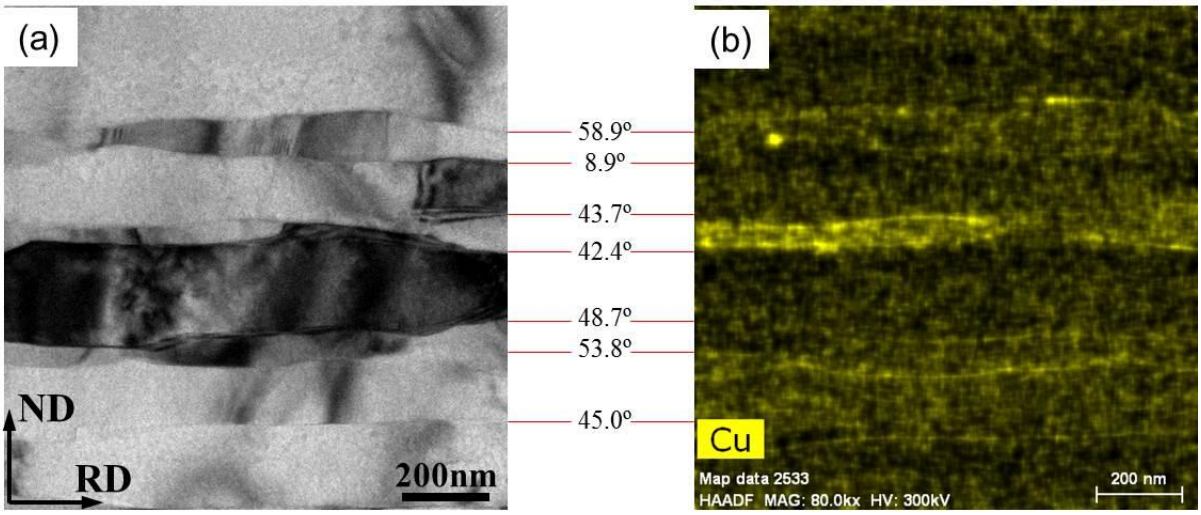

Figure 3. Cu segregation at boundaries in the 98% cold rolled Al-0.3%Cu alloy. (a) TEM bright field image; (b) EDS map of the same area. Misorientation angles of lamellar boundaries are indicated.

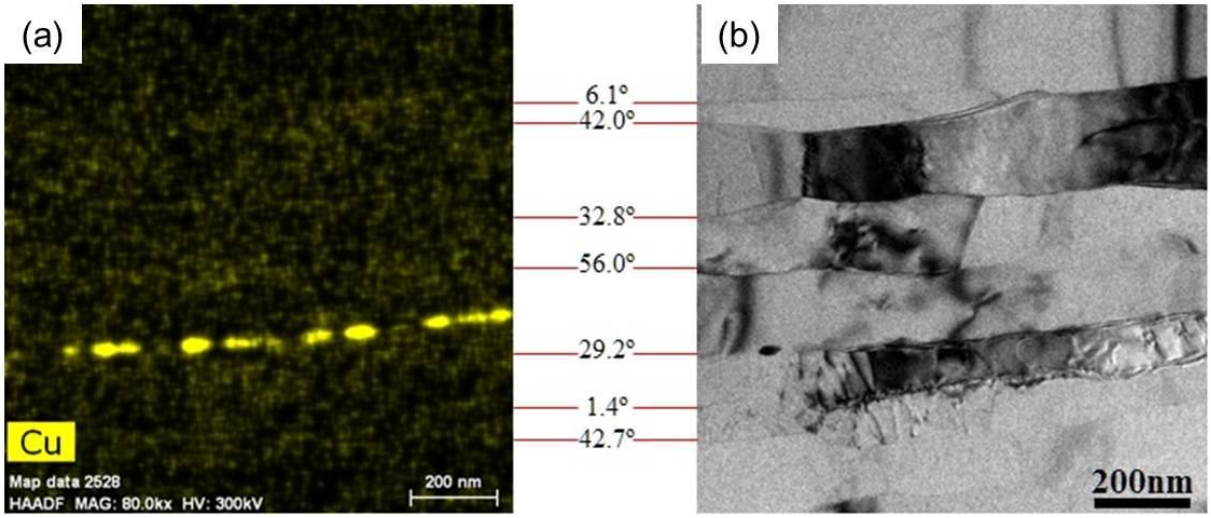

Figure 4. Cu segregation at boundaries in the 98% cold rolled Al-0.3%Cu alloy. (a) EDS map and (b) TEM bright field image of the same area. Misorientation angles of lamellar boundaries are marked.

Figure 4 shows another example of EDS mapping in the 98% cold rolled sample. In this case, most of the lamellar boundaries (both high and low misorientation angles) and all interconnecting boundaries seen in the TEM image cannot be identified on the EDS map. However, along one lamellar boundary (29.2°) clear Cu segregation and even nano-sized precipitates (Al_2Cu) are observed. These observations suggest that the segregation of Cu atoms does not occur at all high angle boundaries, which may be a result of non-uniform distribution of Cu elements at a more global scale in the deformed sample.

To further illustrate the Cu segregation at the lamellar boundaries, the 98% deformed sample was annealed at 200°C for 1 hour. Figure 5 shows the SEM-BSE image of the annealed sample. Compared with the as deformed state (figure 1b), many nano-sized second phase particles can be observed in this annealed sample. Most of the particles are aligned along the direction parallel to the RD and associated with the lamellar boundaries. A few particles are seen within the grains but their alignment with the RD indicates that they were formed originally at the lamellar boundaries but left inside the volume after the boundaries moved during the annealing.

The above 3DAP and EDS mapping results showed clearly that the Cu atoms preferred to segregate at the lamellar boundaries in particular the high angle lamellar boundaries. The absence of segregation at low angle lamellar boundaries and interconnecting boundaries suggests that the high misorientation angles enhance the segregation. The preferred segregation of Cu atoms and the occasional formation of nano-sized particles at the high angle lamellar boundaries will play a role in pinning the boundaries and prevent them being removed by triple junction motion during the cold rolling [26], thus chancing the formation of nanoscale lamellar boundaries. Similar pinning effect on the high angle boundaries may occur during annealing, which will in combination with the effect of relatively low mobility of low angle boundaries (without Cu segregation) lead to an enhanced thermal stability.

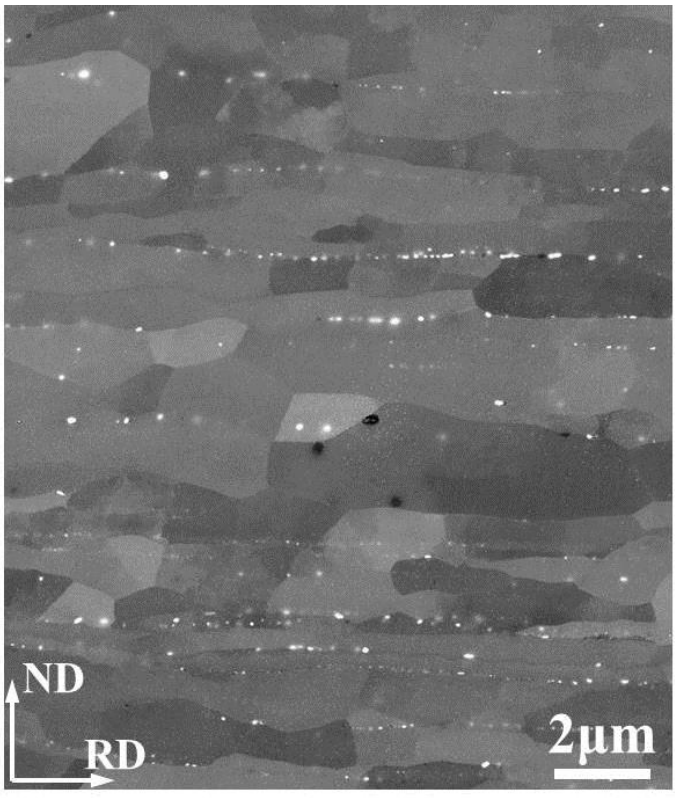

Figure 5. SEM-BSE image of Al-0.3%Cu cold rolled 98% and annealed 200ºC for 1 hour.

4. Conclusions

The distribution of Cu element in an Al (99.9996% purity)-0.3%Cu alloy cold rolled to 98% has been characterized by means of three-dimensional atom probe and ChemiSTEM techniques. The main observations are summarized as follows:

- Segregation of Cu at lamellar boundaries is revealed by both 3DAP and ChemiSTEM techniques. The Cu concentration at segregated boundaries can be as high as 7wt.%, which is about 20 times of the nominal concentration of the alloy.
- High segregation of Cu element is only found at high angle lamellar boundaries, while low angle lamellar boundaries and interconnecting dislocation boundaries do not show obvious Cu segregation, indicating that boundary misorientation angles play a role in enhancing the segregation of Cu.

Acknowledgments

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References

[1] Meyers M, Mishra A and Benson D 2006 *Prog. Mater. Sci.* **51** 427–556
[2] Valiev R Z and Zhu Y 2015 *Research Society of Japan* **40** 309–18
[3] Yu C, Kao P and Chang C 2005 *Acta Mater.* **53** 4019–28
[4] Lu K, Lu L and Suresh S 2009 *Science* **324** 349–52
[5] Huang X, Tsuji N and Pantleon W 2009 *Risoe International Symposium on Materials Science* **30** 59–80
[6] Huang T, Dong Q, Gong X, Hansen N, Liu Q and Huang X 2012 *J. Mater. Sci.* **47** 7914–20
[7] Huang T, Li C, Wu G, Yu T, Liu Q, Hansen N and Huang X 2014 *J. Mater. Sci.* **49** 6667-73
[8] Huang T, Wu G, Liu Q and Huang X 2014 *Mater. Sci. Forum* **783-786** 2629-34
[9] Cheng S, Zhao Y, Zhu Y and Ma E 2007 *Acta Mater.* **55** 5822-32
[10] Song R, Ponge D, Raabe D and Kaspar R 2005 *Acta Mater.* **53** 845-58
[11] Song R, Ponge D and Raabe D 2005 *Scripta Mater.* **52** 1075-80
[12] Liu G, Zhang G, Jiang F, Ding X, Sun Y and Sun J, et al. 2013 *Nat. mater.* **12** 344-50
[13] Zhao Y, Liao X, Cheng S and Ma E 2006 *Adv. Mater.* **18** 2280-3
[14] Huang T, Wu G, Huang X and Hansen N 2015 *IOP Conf. Series: Materials Science and Engineering* **89** 012028
[15] Zhang H, Lu K, Pippan R, Huang X and Hansen N 2011 *Scripta Mater.* **65** 481–4
[16] Jiang L, Li J, Cheng P, Liu G, Wang R, Chen B, Zhang J, Sun J, Yang M and Yang G 2014 *Scientific reports* **4** 3605
[17] Li X, Wakeel A, Huang T, Wu G and Huang X 2015 *IOP Conference Series: Materials Science and Engineering* **89** 012032
[18] Wakeel A, Huang T, Wu G, Mishin O V and Huang X 2015 *IOP Conference Series: Materials Science and Engineering* **82** 012050
[19] Liu Q 1995 *Ultramicroscopy* **60** 81-9
[20] Tsuji N, Ito Y, Saito Y and Minamino Y 2002 *Scripta Mater.* **47** 893-9
[21] Tsuji N, Saito Y, Lee S and Minamino Y 2003 *Adv. Eng. Mater.* **5** 338-44
[22] Huang X, Hansen N and Tsuji N 2006 *Science* **312** 249-51
[23] Kidmose J 2014 PhD Thesis, *Technical University of Denmark*
[24] Kamikawa N, Huang X, Tsuji N and Hansen N 2009 *Acta Mater.* **57** 4198-208
[25] Araullo-Peters V, Gault B, Shrestha S and Yao L, et al. 2012 *Scripta Mater.* **66** 907-10
[26] Yu T, Hansen N, Huang X and Godfrey A 2014 *Mater. Res. Lett.* **2** 160-5